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学位論文要旨

Abstract

A new technique for separating trace vaporous and gaseous components (AMCs) from carrier gases was proposed, which utilizes preferential ionization and electrical migration of ions.

Nitrogen and oxygen flow containing toluene vapor was divided into two flows, while the flow was irradiated with alpha-ray or soft X-ray under the electrical field. The ionized toluene molecules in one flow electrically migrated into the other flow causing toluene rich and free carrier gas flows. The maximum separation efficiency of the improved separator was 67% from the nitrogen gas containing toluene vapor of 0.15ppm. The dependency of toluene separation efficiency on the applied voltage was the same as that of cation separation efficiency.

The influence of AMC concentration and the intensity of X-ray irradiation on the separation efficiency was investigated in order to elucidate the separation mechanisms of AMs. Experimental results showed that a higher separation efficiency is attained with a higher intensity of the soft X-ray source and that the separation efficiency increases with decreasing the AMC concentration. The dependency of the AMC separation efficiency on these factors was well explained by the proposed separation model, which accounts for the reactions of AMC intermediates and reactive primary cations of carrier gas molecules.

Proposed ionization separation technique was applied to the separation of carbon dioxide. As a result, it was found that carbon dioxide can be separated mostly in the form of anion whereas toluene vapor was separated in the form of cation. The maximum efficiency of electrostatic separation of carbon dioxide was 14% when helium stream contains 2.4 ppm of carbon dioxide at the applied voltage of 600V.

Introduction

Removal of airborne molecular contaminants (AMCs), i.e., vaporous or gaseous contaminants from air and other gases has been of great concern for indoor air quality and semiconductor manufacturing processes. Although AMCs can be removed by adsorption with activated carbons and other sorbents, adsorption method has several drawbacks, e.g., necessity of adsorbent replacement or desorption of adsorbates after adsorption equilibrium and high pressure drop through the adsorption bed. An effective removal technique of AMCs from indoor air and other gases with low energy consumption is required.

Gaseous molecules in the atmosphere are ionized by irradiation with radioactive source, electrical discharge, and combustion, etc. Irradiation of radioactive rays or corona discharge initially generates primary positive ions and free electrons. The free electrons readily attach to electronegative species in air to form negative ions. Since the primary positive and negative ions are unstable, secondary ionization due to ion-molecule reaction occurs by the collisions between ions and neutral species. The ion-molecule reaction is influenced by the external electric fields.

This study proposes a new electrostatic separator of AMC molecules employing a bifurcating flow and low electrical field, which utilizes ion-molecule reaction in ion generation fields. The separation performance of AMC molecules such as toluene and carbon dioxide by the irradiation of alpha-ray and soft X-ray was measured. The effect of the volumetric flow rate on AMC separation efficiency were studied. The ion concentration flowing out from separator was also measured in order to compare the ion separation efficiency with that of AMC. Furthermore, The influence of AMC concentration and the intensity of X-ray irradiation on the separation efficiency was investigated to seek the separation mechanisms of AMCs. The dependency of the AMC separation efficiency on these factors was discussed by a proposed separation model, which accounts for the reactions of AMC intermediates and reactive primary cations of carrier gas molecules.

Ionization Separator

Fig. 1 shows the structure of ionization-separator. Flow containing AMCs is split into two flows, while the flow is being irradiated with alpha-ray from ^{241}Am(2.6MBq) and soft X-ray from Photoionizaer (Model L6941, Hamamatsu Photonics, Japan; energy: 3.0~9.5 keV) under an electric field.

The intensity of soft X-ray can be adjusted by passing the soft X-ray through various numbers of aluminum sheets (aluminum foil, thickness: 12μm), and the intensity of X-ray was measured with a dose meter (ICS-311, Aloka). The soft X-ray generator has a dose rate of 4.7×10^{-6} Gy/s at a distance 1 m away from the source. The dose rate corresponds to the production rate of cations of 2.4×10^{16} $m^{-3}s^{-1}$ at 4 cm away from the source when the generation of a pair of ions requires the energy of 34 eV. In order to find the relationship between the X-ray intensity and the ion generation rate in the separator, we measured the ion concentration at the outlet of separator with an ion counter by changing the relative intensity of X-ray using aluminum sheets. The relationship is shown in **Fig. 2**. As seen in **Fig. 2**, the ion current is not proportional to the intensity of X-ray, and 70 % reduction in the X-ray intensity leads to a decrease in ionization capability by about 46 %.

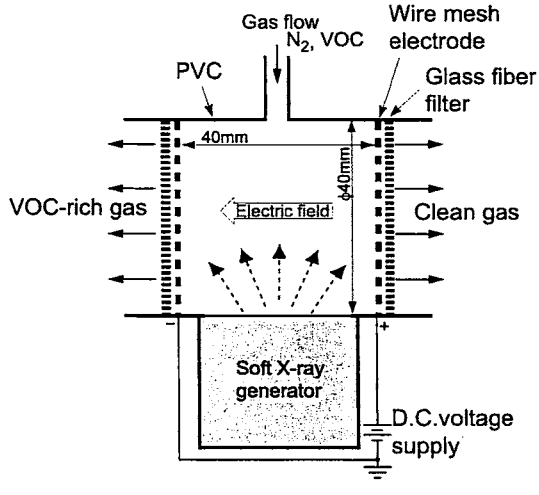

Fig. 1 Schematic of the ionization-separator.

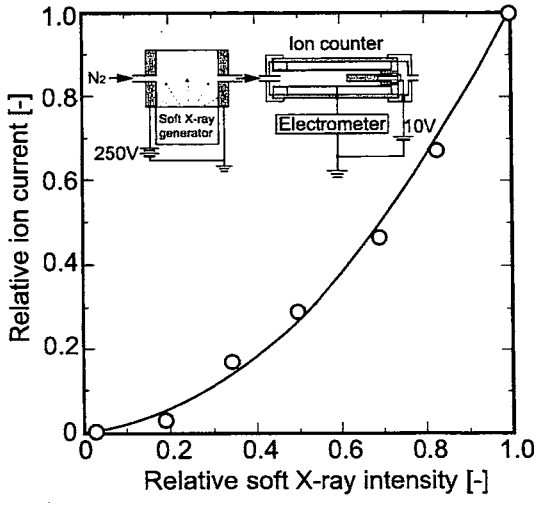

Fig. 2 Soft X-ray intensity versus ion current. N_2 gas flow rate = 1.5L/min.

Experimental Method

Toluene vapor was used as a AMC. Since toluene (proton affinity: 794 kJ/mol, ionization potential 8.82 eV) has a higher proton affinity and smaller ionization potential compared to the nitrogen (proton affinity: 494.5 kJ/mol, ionization potential 15.58 eV), toluene tends to be in the form of cation in an ionization region. Carrier gas of nitrogen (Purity: 99.99995 %, O_2<0.1 ppm, H_2<0.3 ppm, CO<0.1 ppm, CO_2<0.1 ppm, THC<0.1 ppm, H_2O<1 ppm) is further purified by passing it through a liquid-nitrogen cold-trap. The purified nitrogen is mixed with nitrogen containing toluene vapor (13 ppm) to obtain a given concentration, and then introduced into the ionization-separator. Inlet flow is equally divided into two outlet flows, and the inlet and outlet concentrations of toluene vapor are measured by sampling the gas with a gasbag followed by the determination with a gas chromatograph (Shimadzu, GC-17A).

Results and Discussion

Separation of toluene

Fig. 3 shows the ratios of toluene outlet concentration to the inlet concentration as a function of applied voltage. For both the irradiation of soft X-rays and that of alpha-ray, the concentration ratio of the flow from the cathode is larger than unity, while the ratio of the flow from the anode is less than unity, indicating that the separation of toluene occurs in the separator. The ratio of toluene concentration with the soft X-ray is higher than that with the alpha-ray. The concentration ratio curves for cathode outlet and anode are in a mirror image each other with respect to the inlet concentration line (Outlet conc. / Inlet conc. = 1), suggesting that mass balance of toluene holds and therefore no decomposition of toluene takes place in the separator. **Fig. 3** shows that the toluene concentration at the outlet of ionization-separator has a peak and the maximum dimensionless concentration with soft X-ray is 1.3 at the voltage of 600 V.

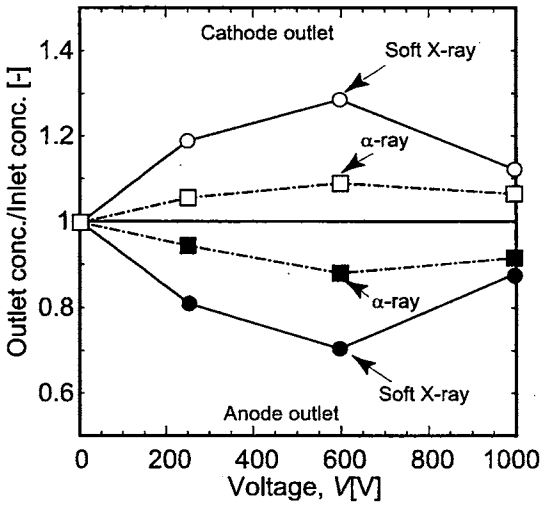

Fig. 3 Change in toluene concentration at the outlet of ionization-separator with applied voltage. Inlet toluene conc. = 500 ppb (1.0L/min.).

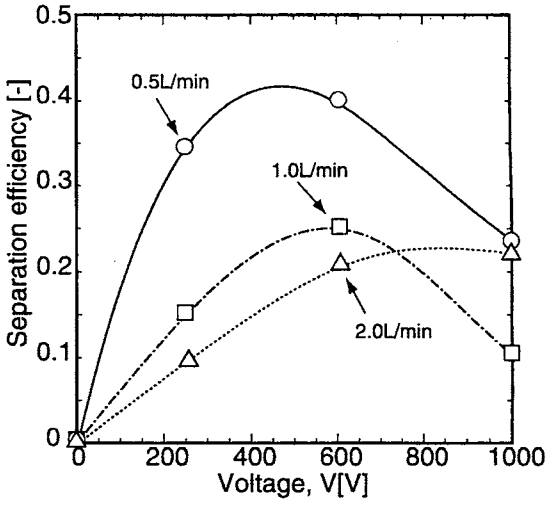

Fig. 4 Influence of volumetric flow rate on toluene separation efficiency. Carrier gas: N_2. Inlet toluene concentration: 0.26ppm

Influence of Flow rate.

Influence of volumetric flow rate on toluene separation efficiency is shown in **Fig. 4** The separation efficiency curves have a peak at a given applied voltage in all cases. As the gas flow rate increases, the separation efficiency peak shifts to a higher voltage. Maximum

separation efficiency increases with decrease in the flow rate. It is considered that effective separation of toluene requires a given residence time for toluene molecules to acquire electrical charge by ion-molecule reaction.

Comparison of toluene separation and cation separation

The cation concentration effluent from cathode outlet was measured by ion-couter. **Fig. 5** shows the comparison of separation efficiency of toluene vapor and that of cation. The separation efficiency of toluene increases with the applied voltage, and attains 0.67 at applied voltage of 1000V. The cation separation efficiency also increases with the applied voltage, and reaches the maximum value at above 600V. The dependency of toluene vapor separation efficiency on the applied voltage is similar to that of cation, indicating that the separation efficiency of toluene in soft X-ray type separator is determined by the cation separation efficiency.

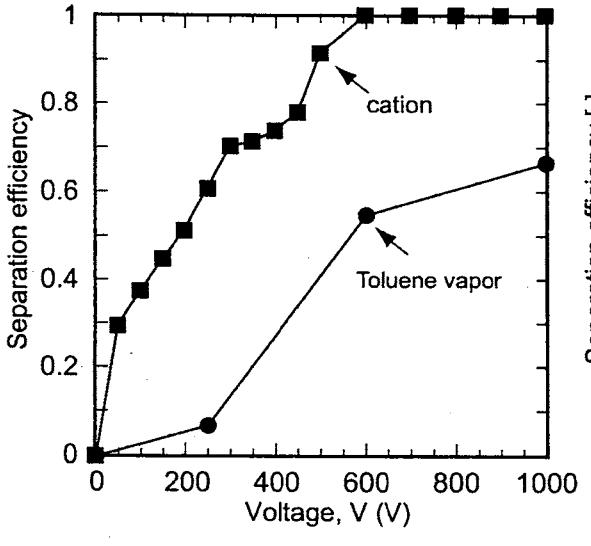

Fig. 5 Comparison of separation efficiency of toluene vapor and that of cation with soft X-ray type separator. Flow rate = 1.5 L/min. Inlet toluene concentration = 0.26 ppm.

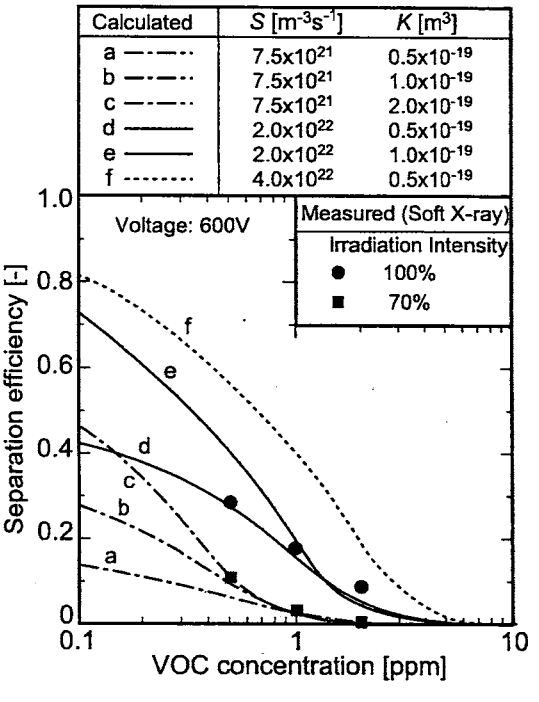

Fig. 6 Change in separation efficiency as a function of the inlet AMC concentration. V = 600 V.

Influence of AMC concentration

Fig.6 shows the change in separation efficiency with the inlet toluene concentration. The separation efficiency of toluene increases with decreasing the inlet toluene concentration, implying that the present separator is more effective for removing a low concentration of AMC. An increase in soft X-ray intensity brings the increased separation efficiency, and the rate of separation efficiency reduction (37 % at 0.5 ppm) is similar to that of ion current (46 %) shown in **Fig. 2**, because the increase in the soft X-ray intensity leads to a higher generation rate of primary bipolar ions which in turn charge toluene molecules

Separation mechanism

Although many ion species are involved even in a binary gas mixture, here we consider only neutral AMC molecules, V, and AMC ions, V^+. When the generation of AMC ions is

proportional to the number of neutral AMC molecules and the depletion of AMC ions is proportional to the number of AMC ions, the mass balance of neutral AMC molecules and AMC ions yields the following one-dimensional convective diffusion equations.

$$\begin{cases} \dfrac{\partial C_{V^+}}{\partial t} = (u - ZE)\dfrac{\partial C_{V^+}}{\partial x} - \alpha C_{V^+} + \beta C_V + D_{V^+}\dfrac{\partial^2 C_{V^+}}{\partial x^2} & (1) \\ \dfrac{\partial C_V}{\partial t} = u\dfrac{\partial C_V}{\partial x} + \alpha C_{V^+} - \beta C_V + D_V\dfrac{\partial^2 C_V}{\partial x^2} & (2) \end{cases}$$

where C is the concentration, u is the flow velocity, D is the diffusion coefficient, α and β are the net depletion rate constant and the net generation rate constant of AMC ions, respectively. Z is the electrical mobility of AMC ions, and E is the electrical field strength. ZE is equal to the ion drift velocity.

In this study, we hypothesize that AMC ions are generated via the reaction intermediates of AMC, which is formed by the collisions of neutral AMC molecules with the reactive primary cations of carrier gas molecules. The generation of AMC cations via the intermediates, V^*, is given by

$$V + X^{+*} \xrightarrow{k_1} V^* + X^+ \xrightarrow{k_2} V^+ + X \quad (3) \quad X^{+*} \xrightarrow{k_3} X^+ \quad (4)$$

where k_1, k_2 and k_3 are the reaction rate constants.

The generation rate of AMC ions, G (= βC_V, in Eqs. (1) and (2)) is given by:

$$G = dC_{V^+}/dt = k_2 C_{V^*} C_{X^+} = \frac{S}{\dfrac{1}{K} + C_V} \cdot C_V \qquad 5)$$

with

$$K = \frac{k_1}{k_3} \qquad 6)$$

where S is the production rate of reactive primary cations, K is the selectivity of AMC ionization over self-ionization of carrier gas by the reactive primary cations. AMC ion generation is given by a function of the production rate of reactive primary cation and inlet AMC concentration.

Unfortunately, no complete set of reaction rates and kinetic constants for this system is available at present. The values of electrical mobility and diffusion coefficient of AMC ions and molecules are assumed to be in the range of those for the atmospheric ions and molecules[1]. the rate constant of α is also assigned to be in the order of 10^3 referring to the previous work[2]. The unknown values of S and K are varied parametrically for fitting the experimental data.

Fig. 6 also compares the dimensionless outlet concentration calculated for various values of S and K with the experimental data. As shown in the figure, S determines the AMC concentration at which the separation of AMC takes place, whereas K affects the increasing rate of outlet concentration with the decrease in AMC concentration. The values of S which give the best fit for the experimental data are 2.0×10^{22} and 7.5×10^{21} $m^{-3}s^{-1}$ respectively for 100 and 70 % of X-ray intensity. The reduction in S due to the decrease in X-ray intensity nearly corresponds to the ion concentration reduction due to the X-ray intensity reduction shown in **Fig. 2**. The values of S which give the best fit for the experimental data are in the order of 10^{21}~10^{22} $m^{-3}s^{-1}$, which is five to six orders of magnitude higher than that predicted by the X-ray intensity (2.4×10^{16} $m^{-3}s^{-1}$ at 4 cm away from the source). The big discrepancy might be attributed to the involvement of reactive species other than reactive cations of carrier gas molecules in the ionization of AMC molecules.

Separation of carbon dioxide

Proposed ionization separation technique was applied to the separation of carbon dioxide.In order to evaluate the separation performance of ionization-separator for CO_2 taking into account the decomposition by the irradiation of soft X-ray during the separation, we defined the CO_2 relative concentration from the separator as $C^* = C/C_{V=0}$, where C is the outlet concentration with soft X-ray irradiation and the applied voltage, and $C_{V=0}$ is the outlet concentration with soft X-ray irradiation without the applied voltage. **Fig.7** shows the influence of applied voltage on the relative concentration of CO_2 at the inlet CO_2 concentrations of 2.4 and 4.4 ppm in helium flow. CO_2 concentration is slightly higher than the inlet concentration when the ground electrode is anode and it is considerably lower when it is cathode, indicating that the separation of CO_2 does occur. We can see from **Fig.7** that the migration of CO_2 in a form of anion is dominant in the separator whereas toluene vapor was separated in the form of cation. The CO_2 relative concentration has a minimum and maximum at the voltage of 600V and -600V for both inlet concentrations, which is in agreement with the voltage at which the maximum separation of toluene was attained.

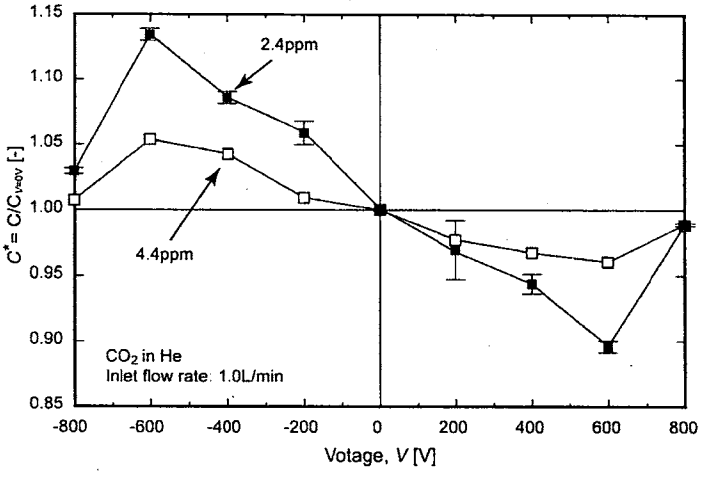

Fig. 7 Change in the relative concentration of CO_2 as a function of applied voltage.

Conclusiion

This study proposed a new electrostatic separator for airborne molecular contaminants (AMC) molecules from various carrier gases. The separation mechanism is such that AMC molecules are ionized via ion-molecule reaction in ion generation fields and are at the same time concentrated into one flow of bifurcating flow by applied electrical field. The separation efficiencies of AMCs have been studied experimentally and theoretically. The following results were obtained:

(1) Toluene molecules were electrostatically separated by alpha-ray ionization and soft X-ray photo-ionization. Toluene separation efficiency has a peek at a given applied voltage. The maximum separation efficiency of the improved separator was 67% from the nitrogen gas containing toluene vapor of 0.15ppm.

(2) The separation efficiency of toluene was determined by the separation efficiency of cations, although the measured ion concentration was large order of magnitudes lower than the number of separated toluene molecules

(3) The experimental separation efficiency of AMCss increased with decreasing the inlet concentration. The dependencies of the separation efficiency on the applied voltage and inlet AMC concentration are successfully explained by the present separation model, which accounts for the reactions of AMC intermediates and reactive primary cations of carrier gas molecules.

(4) The proposed ionization separation technique was applied to the separation of CO_2. CO_2 molecules in a helium was separated mostly in the form of anion by the ionization separator. The CO_2 concentration relative to the outlet concentration without applied voltage increased with decreasing the inlet concentration, as found in the separation of toluene. Maximum relative concentration of CO_2 was 1.14 in helium carrier gas containing 2.4 ppm CO_2 at an applied voltage of 600V.

Reference

(1) Adachi, M., Kousaka, Y., Okuyama, K.; "Unipolar and Bipolar Diffusion Charging of Ultrafine Aerosol Particles", *J. Aerosol Sci.* **16** (2), 109-123 (1985)

(2) Iinuma, K.; "Analysis of Reactive Ion Transport in Weakly Ionized Gas Mixtures", *Can. J. Chem.*, **69**, 1090-1099 (1991)

学位論文審査結果の要旨

平成16年7月5日に在学期間短縮の可否を判定するため、予備審査会を開催して、口頭発表と質疑応答、ならびに提出予定学位論文、参考論文、副論文を審査した。本学自然科学研究科博士後期課程在籍期間中に、掲載決定の論文を含め審査付き論文が4編あること、また、参考論文、副論文合わせて8編の研究業績がありその研究内容も極めて優れていることから、在学期間を短縮して博士の学位を申請可能と判断した。

その後、平成16年7月27日に口頭発表と質疑応答を行い、引き続き開催した論文審査会において以下のように決定した。

本論文は、気中の分子状汚染物質（AMC）の分離に関して、放射性同位元素ならびに軟X線を用いた両極イオン生成場で揮発性有機化合物（VOC）を選択的にイオン化すると同時に電界を印加することにより、キャリアガスからVOCを直接分離できることを見出した。この研究成果は、米国化学会が発行する二つの雑誌（Environmental Science and Technology, Industrial&Engineering Chemistry Research）に掲載され、国内外から高い評価を得ている。さらに、本分離法がVOCだけでなく、ガス状物質CO_2の分離にも適用できることを示し、蒸気状・ガス状極低濃度汚染物質の汎用かつ有効な分離法としてイオン化静電分離法を確立した。

以上のように，本論文は，新しい気中からの分子状汚染物質の直接分離法を提案し、分離の機構を解明したものであり、工学的な価値は極めて高く，博士（工学）の学位を授与するに値すると判断する。